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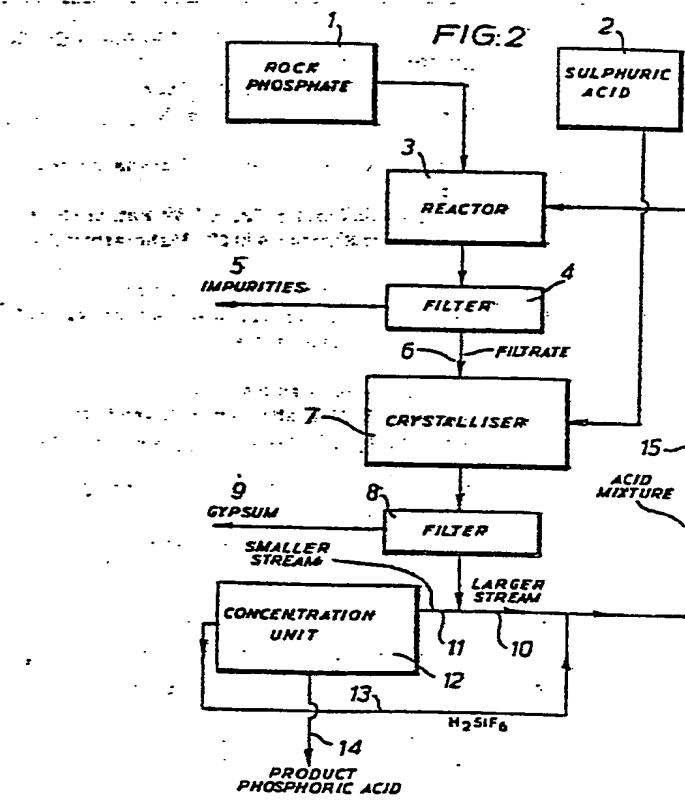
⑲ A process to manufacture commercially acceptable phosphoric acid and gypsum from rock phosphate.

⑳ The present invention provides a process for the manufacture of gypsum and phosphate from rock phosphate, the process comprises solubilising the phosphate and fluoride content of rock phosphate by treating it with fluosilicic acid (H_2SiF_6) optionally together with phosphoric acid in a reactor (3), treating the solution so obtained, optionally after filtration in unit (4), with sulphuric acid in a crystalliser (7) to precipitate gypsum and regenerate fluosilicic acid, filtering the slurry to remove gypsum, dividing the remaining liquor into two portions, the major portion (10) being recycled to treat further rock phosphate, the minor portion being treated to remove the phosphoric acid content thereof in unit (12). The removed phosphoric acid constitutes the product of the process and fluosilicic acid remaining in the minor portion is recycled to treat further rock phosphate.

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A process to manufacture commercially acceptable phosphoric acid and gypsum from Rock Phosphate.

This invention relates to a process to manufacture commercially acceptable phosphoric acid and gypsum from Rock Phosphate.

The starting material to manufacture Phosphoric Acid is Rock Phosphate. The Rock Phosphate coming from different countries has varying (from 20 to 30 per cent) proportions of P_2O_5 content. Samples of Rock Phosphate which come from Morocco, Tunisia, Jordan, Senegal and United States of America have a higher percentage of P_2O_5 than those which come from countries like India. The Principal impurities are silica, iron and aluminium oxides designated as R_2O_3 . (This is also called FERAL impurities).

The existing process for the manufacture of Phosphoric Acid employ samples of Rock Phosphate richer in P_2O_5 content. The existing processes comprise reacting finely ground Rock Phosphate powder with Sulphuric Acid giving Phosphoric Acid and Gypsum (Calcium Sulphate 15 Dihydrate and/or hemi-hydrate) along with impurities consisting of silica and fluorine compounds. The product gypsum will require further purification.

Some samples of Rock Phosphate are difficult to grind to a fine powder owing to hard silica impurities and they are not preferred for the practice of existing processes because the grinding procedure becomes expensive.

This invention provides a process for the manufacture of commercially acceptable Phosphoric Acid and Gypsum from any sample of Rock Phosphate (P_2O_5 - rich or poor) without appreciable evolution of gaseous fluorine at the reaction stage. A striking feature of this process is the complete solubilisation of the P_2O_5 and fluorine contents of the sample of Rock Phosphate. The Fluorine content of the liquor could be utilised for the purpose of obtaining fluorine-based compounds of great commercial value like SF_5 , AlF_3 and Cryolite.

This invention provides a process to manufacture from Rock Phosphate commercially acceptable Phosphoric Acid and Gypsum comprising reacting coarser samples of Rock Phosphate with a mixture of Phosphoric Acid and Fluosilicic Acid with a minute quantity of Sulphuric Acid at a temperature from ambient to $100^{\circ}C$. until the Phosphate and Fluorine contents of the Rock Phosphate are substantially dissolved, the resulting slurry being fed into a crystalliser containing slurry from previous batch, the slurry being reacted in the crystalliser with sulphuric acid, the reaction in the crystalliser being continued till gypsum crystal-formation is complete, the crystalliser contents being filtered and the residue containing a substantially gypsum crystals being washed several times with 20l each liquors and water, the filtrate and washings, containing a mixture of phosphoric acid and fluosilicic acid, being divided into two unequal portions, the smaller portion containing P_2O_5 "equivalent" to that contained in the Rock Phosphate at the beginning of the process, the smaller portion being concentrated to give phosphoric acid, the fluosilicic acid evolved during the concentration process being scrubbed and mixed with the larger portion, the last-mentioned mixture being recycled to a fresh quantity of Rock Phosphate to repeat the process.

In an embodiment of this invention, the aforesaid slurry produced by the reaction of Rock Phosphate with the mixture of Phosphoric Acid and Fluosilicic Acid with a minute quantity of Sulphuric Acid is filtered to remove the insoluble impurities and the filtrate and washings of the residue with leach liquor and water are fed into the crystalliser containing slurry from previous batch. This embodiment gives purer gypsum crystals.

In another embodiment of this invention, the aforesaid slurry produced by the reaction of rock-phosphate with a mixture of phosphoric acid and fluosilicic acid with a minute quantity of sulphuric acid is filtered and the filtrate and washings of the residue by leach liquor and water are divided into two portions, the smaller portion containing P_2O_5 "equivalent" to that contained in the rock-phosphate at the beginning of the process, the smaller portion being concentrated, cooled and filtered, the residue being wet calcium silicofluoride and the filtrate being the product phosphoric acid, the cake of the wet calcium silicofluoride along with the aforesaid larger portion being added into a crystalliser containing slurry from previous batch and sulphuric acid being added into the crystalliser, the reaction being continued till the gypsum crystal-formation is complete, the gypsum crystals being filtered out leaving as filtrate a mixture of phosphoric acid and fluosilicic acid, which mixture is recycled to a fresh quantity of rock-phosphate to initiate the process. This embodiment gives purer gypsum crystals.

The foregoing three processes are applicable to all types of samples of rock phosphate, whatever their P_2O_5 content, which is generally varying from 20 to 30 per cent. These processes give a quality of gypsum with respect to P_2O_5 impurity that it can be used, without further purification,

in the manufacture of plasterboard or as an additive in the manufacture of cement. The processes claimed in claims 2 and 3 give gypsum containing less than 0.3 per cent P_2O_5 and such sample of gypsum is suitable as a whitener in the paper industry.

5 A further advantage of these processes is the almost complete recovery of the fluorine content of the rock phosphate.

This invention is now illustrated with reference to the accompanying three flow-sheets by the following six examples. The examples 1 and 2 read with flow sheet 1 illustrate the process claimed in claim 1 with rock phosphate samples respectively rich and poor in P_2O_5 content. Examples 3 and 4 read with flow sheet 2 likewise illustrate the process claimed in claim 2 with rock phosphate samples respectively rich and poor and in P_2O_5 content. Examples 5 and 6 read with flow sheet 3 illustrate the process claimed in claim 3 with rock phosphate samples respectively rich and poor in P_2O_5 content. These examples do not in any way limit the full ambit of the claims.

EXAMPLE 1 :

A sample (1) was taken of 200 gms of low grade unbeneficiated coarse rock phosphate of particle size of -8 to +25 mesh. On analysis the sample showed the following composition :

P_2O_5	:	33.00 %
CaO	:	45.20 %
F	:	3.2 %
SiO_2	:	15.00 %
$Fe_2O_3 + Al_2O_3$:	2.40 %
CO_2	:	1.00 %
NaCl	:	0.1 %
SO_3	:	0.4 %

The said sample was reacted in a well stirred reactor (3) with 2090 gms of acid mixture containing 20% w/w P_2O_5 , 11.91% w/w H_2SiF_6 , 0.5% w/w H_2SO_4 at $70^{\circ}C$. for a period of 2 hours. The slurry obtained, without filtration and 155 gms of 98.5% w/w H_2SO_4 (2) were simultaneously fed into a well stirred crystalliser (4) containing slurry from previous batch, at $65^{\circ}C$. for 3 hours. After the reaction, the resulting slurry was passed through the filter (5) and washed several times with leach liquors and water to give 430 gms of wet gypsum cake along with silica mud and other insoluble impurities. The washed residue (6) was "Product" gypsum ($CaSO_4 \cdot 2H_2O$) of a grade acceptable in the manufacture of cement. The aggregate filtrate weighing 2265 gms. comprised of acid mixture containing 21.28% w/w P_2O_5 , and 11.3% w/w H_2SiF_6 . This aggregate filtrate (2265 gms) was divided into two portions - one (8) weighing 301 gms and the other (7) weighing 1964 gms, the smaller portion (8) weighing 301 gms. was concentrated in the concentration unit (9) 15 to get 121 gms of "Product" Phosphoric Acid (11), containing 52% w/w P_2O_5 and 180 gms of liquor (10) containing 17.0% w/w H_2SiF_6 by scrubbing and recycling it. The recovery of H_2SiF_6 was 90%. The 180 gms of liquor (10) was separately concentrated to get 136 gms liquor containing 21.41% w/w H_2SiF_6 , of which 126 gms were added to the portion (7) containing 1964 gms 20 of the aforesaid filtrate to get 2090 gms of acid mixture (12) for being recycled to the reactor (3) for a fresh sample of 200 gms of rock phosphate. The recovery of P_2O_5 from rock phosphate to "Product" phosphoric acid was 95%.

EXAMPLE 2 :

25 A sample (1) was taken of 200 gms of low grade unbeneficiated coarse rock phosphate of particle size of -8 +25 mesh. On analysis the sample showed the following composition :

P_2O_5	:	20.04 %
CaO	:	26.65 %
$Fe_2O_3 + Al_2O_3$:	4.77 %
F	:	2.00 %
SiO_2	:	42.32 %
LOI at 1000°C.	:	2.89 %

The said sample was reacted in a well stirred reactor (3) with 1263 gms of acid mixture containing 20.0% W/W P_2O_5 , 11.96% H_2SiF_6 and 0.5% W/W H_2SO_4 at 70°C. for a period of two hours. The slurry obtained, without filtration and 92 gms of 98.5% W/W H_2SO_4 (2) were simultaneously fed into a well stirred crystalliser (4) containing slurry from previous batch, at 65°C. for 3 hours. After the reaction, the resulting slurry was passed through the filter (5) and washed several times ^{with each liquors and water} to give 350 gms. of wet gypsum cake along with silica mud and other soluble impurities. The washed residue (6) was "Product" gypsum ($CaSO_4 \cdot 2H_2O$) of a grade acceptable in the manufacture of cement. The aggregate filtrate weighing 1380 gms. comprised of acid mixture containing 21.09% W/W P_2O_5 and 11.26% W/W H_2SiF_6 . This aggregate filtrate (1380 gms) was divided into two portions: one (8) weighing 182 gms and the other (7) weighing 1198 gms. The smaller portion (8) weighing 182 gms. was concentrated in the concentration unit (9) to get 72 gms of "Product" phosphoric acid (11) containing 52% W/W P_2O_5 and 110 gms. of liquor containing 16.76% W/W H_2SiF_6 (10) by scrubbing and recycling it. The recovery of H_2SiF_6 was 90%. The 110 gms of liquor (10) was separately concentrated to get 70 gms. liquor containing 24.87% W/W H_2SiF_6 , of which 65 gms. were added to the portion (7) containing 1198 gms of the aforesaid filtrate to get 1263 gms of acid mixture (12) for being recycled to the reactor (3) for a fresh sample of 200 gms of rock phosphate. The recovery of P_2O_5 from rock phosphate to "Product" Phosphoric Acid was 93%.

The following two examples illustrate the second embodiment of this invention. The rock phosphate sample in example 3 has a higher percentage of P_2O_5 than the sample in example 4. The bracketed numeral references are to the accompanying sheet No.2.

5 EXAMPLE 3 :

A sample (1) of 200 gms. of low grade unbeneficiated coarse rock phosphate from Jhabua Mines in Madhya Pradesh of the particle size of -8 to +25 mesh showed on analysis the following composition :

	P_2O_5	:	33.00 %
10	CaO	:	45.20 %
	F	:	3.2 %
	SiO_2	:	15.00 %
	$Fe_2O_3 + Al_2O_3$:	2.40 %
	CO_2	:	1.00 %
15	NaCl	:	0.1 %
	SO_3	:	0.4 %

The said sample was reacted in a well stirred reactor (3) with 2090 gms of acid mixture containing 20.0% w/w P_2O_5 , 11.91% w/w H_2SiF_6 and 0.5% w/w H_2SO_4 at 70°C. for a period of two hours. The resulting slurry was 20 passed through the filter (4) to remove 130 gms. of wet insoluble impurities (5) comprising quartz, mud, earthy matter and crude gypsum. The impurities were washed several times with leach liquors and water, and the filtered washings were added to the filtrate (6). The aggregate filtrate (6) weighing 2260 gms. contained in solution practically 98% phosphate and 95% of the fluorine content of the rock phosphate (1). Analysis of the filtrate gave 21.357% w/w P_2O_5 , 11.354% w/w H_2SiF_6 . The said 2260 gms. of filtrate (6) and 155 gms. of 98.5% w/w H_2SO_4 (2) were simultaneously

fed into a well stirred crystalliser (7) containing slurry from previous batch at the temperature 65°C. for 3 hours. After the reaction, the resulting slurry was passed through filter (8) and the residue (9) was washed with leach liquors and water and filtered several times. The washed residue (9) was 300 gms. of wet cake of "product" gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) of a grade acceptable in the manufacture of cement. The aggregate filtrate weighing 2265 gms. comprised acid mixture containing 21.28% W/W P_2O_5 and 11.273% W/W H_2SiF_6 . The aggregate filtrate (2265 gms) was divided into two portions : One (11) weighing 300 gms and the other (10) weighing 10 1965 gms. The smaller portion (11) weighing 300 gms were concentrated in the concentration unit (12) to get 121 gms. of "Product" phosphoric acid (14) containing 52% W/W P_2O_5 and 179 gms. of liquor (13) containing 17.01% W/W H_2SiF_6 by scrubbing and recycling it. The recovery of H_2SiF_6 was 90%. The 179 gms. of liquor (13) was separately concentrated to get 15 132 gms. of liquor containing 21.92% W/W H_2SiF_6 of which 125 gms. were added to the portion (10) containing 1965 gms. of aforesaid filtrate to get 2090 gms. of acid mixture (15) for being recycled to the reactor (3) for a fresh sample of 200 gms. of rock phosphate. The recovery of P_2O_5 from rock phosphate to "Product" phosphoric acid was 95%.

20 EXAMPLE 4 :

A sample (1) of 200 gms. of low grade unbeneficiated coarse rock phosphate from Jhabua mines in Madhya Pradesh of particle size of -8 to +25 mesh showed on analysis the following composition :

P_2O_5	:	20.04 %
CaO	:	26.65 %
$Fe_2O_3 + Al_2O_3$:	4.77 %
F	:	2.00 %
5		
SiO_2	:	42.32 %
LOI at 1000°C	:	3.89 %

The said sample was reacted in a well stirred reactor (3) with 1263 gms. of acid mixture containing 20.0% w/w P_2O_5 , 11.96% w/w H_2SiF_6 and 0.5% w/w H_2SO_4 at 70°C. for a period of 2 hours. The resulting slurry was passed 10 through the filter (4) to remove 170 gms. of wet insoluble impurities (5) comprising quartz, mud, earthy matter and crude gypsum. The impurities were washed several times ^{with leach liquors and water} and the filtered washings were added to filtrate (6). The aggregate filtrate (6), weighing 1393 gms. contained in solution practically 96% phosphate and 90% fluorine content of the 15 rock phosphate (1). Analysis of the filtrate gave 20.9% w/w P_2O_5 and 11.17% w/w H_2SiF_6 . The said 1393 gms of filtrate (6) and 92 gms. of 98.5% w/w H_2SO_4 (2) were simultaneously fed into a well stirred crystalliser (7) containing slurry from previous batch, at 65°C. for 3 hours. After the reaction the resulting slurry was passed through filter (8) 20 ^{with leach liquors and water} and the residue (9) was washed ^{and} filtered several times. The washed residue (9) was 180 gms. of wet cake of "Product" gypsum ($CaSO_4 \cdot 2H_2O$) of a grade acceptable in the manufacture of cement. The aggregate filtrate weighing 1382 gms comprised of acid mixture containing 21.037% w/w P_2O_5 and 11.234% w/w H_2SiF_6 . The aggregate filtrate (1382 gms) was 25 divided into two portions - one (11) weighing 181 gms. and the other (10) weighing 1201 gms. The smaller portion (11) weighing 181 gms. was

concentrated in the concentration unit (12) to get 72 gms of "Product" phosphoric acid (14), containing 52% w/w P_2O_5 , and 109 gms of liquor (13) containing 16.789% w/w H_2SiF_6 by scrubbing and recycling it. The recovery of H_2SiF_6 was 90%. The 109 gms of liquor (13) was separately concentrated to get 67 gms liquor containing 26.024% w/w H_2SiF_6 of which 62 gms were added to the portion (10) containing 1201 gms of the aforesaid filtrate to get 12±3 gms of acid mixture(15) for being recycled to the reactor (3) for a fresh sample of 200 gms of rock phosphate. The recovery of P_2O_5 from rock phosphate to "Product" phosphoric acid was 93%.

10 EXAMPLE 5 :

200 gms. of unbeneficiated coarse Rock Phosphate (1) with particle size -8 to +25 mesh from Jhabua mines of Madhya Pradesh (India) was selected which, on analysis, showed the following composition:-

15	P_2O_5	:	33 %
	CaO	:	45.20 %
	F	:	3.20 %
	SiO_2	:	15 %
	$Fe_2O_3 + Al_2O_3$:	2.40 %
	CO_2	:	1.00 %
20	NaCl	:	0.10 %
	SO_3	:	0.40 %

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The Rock Phosphate sample was reacted with 2090 gms. of acid mixture containing 20.0% P_2O_5 W/W, 11.91% H_2SiF_6 W/W and 0.5% H_2SO_4 W/W at $70^{\circ}C$. for a period of 2 hours in a well stirred reactor (3). The slurry was filtered in filter (4) to remove 130 gms. of wet insoluble impurities 5 comprising quartz, mud, earthy matter and gypsum (5). The filtrate and washings weighing 2260 gms. contained practically 98% Phosphate and 95% Fluorine content of the Rock Phosphate, in solution. Analysis of the filtrate gave

$$P_2O_5 = 21.357 \% \text{ W/W}$$

10 Fluorine expressed as H_2SiF_6 = 11.354 % W/W

This mass of filtrate and washings was divided into two streams : Stream (6) of 1860 gms. and stream (7) of 400 gms. The stream (7) was concentrated by vacuum evaporation (9) at 10 mm of mercury pressure and $80^{\circ}C$. 15 temperature. When the P_2O_5 reached a level of 45% W/W, crystalline calcium silico fluoride dihydrate, $CaSiF_6 \cdot 2H_2O$ was thrown out. The slurry was cooled (11) to room temperature and filtered. It gave 85 gms. of wet crude cake (14) of crystalline calcium silico fluoride dihydrate and 140 gms. of product phosphoric acid (13) containing 45% P_2O_5 W/W in 20 the filtrate. A total quantity of 175 gms. of water (10) was distilled off in the above process. The recovery of P_2O_5 from Rock Phosphate to product acid was about 95%.

The 85 gms. cake (14) of wet crude, crystalline, calcium silico fluoride dihydrate, $CaSiF_6 \cdot 2H_2O$, was then added into a well stirred crystalliser (8) 25 along with the major stream (6), containing 1860 gms. of the aforesaid filtrate from the earlier stage (4) and was reacted with 155 gms. of 98.5%

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W/W H_2SO_4 (2) which was simultaneously added to the same crystalliser (8) at $65^{\circ}C$. temperature, during a course of 3 hours. On filtration and washing (15), this reaction gave 300 gms. of wet gypsum cake, $CaSO_4 \cdot 2H_2O$ (16). This gypsum was dazzling white in colour and contained a maximum of 0.3% P_2O_5 and 0.2% F impurities on dry basis. This is of a quality as desired for its use in cement manufacture. This step also resulted in a filtrate comprising 2000 gms. of acid containing 20.9% W/W P_2O_5 and 12.54% W/W H_2SiF_6 . This filtrate after suitable dilution with 90 ml wash water resulted in 2090 gms. of recycle acid containing 20% W/W P_2O_5 and 12.0% W/W H_2SiF_6 .

10 The said mixture was recycled (17) to the reactor (3) for a fresh lot of 200 gms. of Rock Phosphate.

EXAMPLE 6 :

In this example, the Rock Phosphate selected has a lower percentage of P_2O_5 and a higher percentage of silica than in the example 1.

15 200 gms. of low grade unbeneficiated coarse Rock Phosphate (1) from Jhabua mines of Madhya Pradesh (India) with particle size -8 to +25 mesh and containing high silica impurities and low P_2O_5 and other constituents as specified in the analysis given below:-

20	P_2O_5	:	20.04 %
	CaO	:	26.65 %
	$Fe_2O_3 + Al_2O_3$:	4.77 %
	F	:	2.00 %
	SiO_2	:	42.32 %
	LOI at $1000^{\circ}C$.	:	2.89 %

was reacted with 1263 gms. of recycled acid mixture containing 20% W/W P_2O_5 , 11.96% W/W H_2SiF_6 and 0.5% W/W H_2SO_4 at $70^{\circ}C$. for a period of 2 hours in a well stirred reactor (3). The slurry was filtered in filter (4), to remove 170 gms. of wet insoluble impurities comprising quartz, mud, earthy matter and gypsum (5). The filtrate and washings weighing 1393 gms contained practically 96% phosphate and 90% fluorine content of the Rock Phosphate in solution. The analysis of the filtrate gave :

P_2O_5 : 20.90 % W/W

Fluorine expressed as

H_2SiF_6 : 11.17 % W/W

This mass of filtrate and washings was divided into two streams : Stream (6) containing 1153 gms. and stream (7) containing 240 gms. The stream (7) was then subjected to concentration by vacuum evaporation (9) at 10 mm of mercury pressure and $80^{\circ}C$. temperature. When the concentration of P_2O_5 reached a level of 45% W/W, crystalline calcium silicofluoride dihydrate $CaSiF_6 \cdot 2H_2O$, was thrown out. The slurry was cooled (11) to room temperature and filtered (12) off to give 50 gms. of wet crude cake (14) of crystalline calcium silicofluoride dihydrate and 83 gms. of Phosphoric Acid (13) containing 45 per cent P_2O_5 W/W in the filtrate as the product sought by this invention. A total quantity of 107 gms. of water (10) was distilled off in the above process. The recovery of P_2O_5 from Rock Phosphate to product phosphoric acid was about 93%. The 50 gms. cake (14) of wet crude crystalline calcium silicofluoride dihydrate,

$\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$, was then added into a well stirred crystalliser (8) along with the major stream (6) containing 1153 gms. of the aforesaid filtrate from the earlier stage and was reacted with 94 gms. of 98.5% w/w H_2SO_4 (2) which was simultaneously added to the same crystalliser at 65°C . temperature during a course of

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3 hours. On filtration and washing (15) this reaction gave 180 gms. of wet gypsum cake, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (16). This gypsum was dazzling white in colour and contained a maximum of 0.3% P_2O_5 and 0.2% F as impurities on dry basis. Such gypsum is of a quality as desired for its use in cement manufacture.

5 This last step also resulted in a filtrate comprising 1238 gms. of acid containing 20.425% P_2O_5 and 12.207% W/W H_2SiF_6 . The said filtrate after suitable dilution with 25 ml. of wash water resulted in 1263 gms. of acid mixture containing 20.0% W/W P_2O_5 and 11.96% W/W H_2SiF_6 . The said mixture was recycled to the reactor (3) for a fresh lot of 200 gms. of Rock

10 Phosphate.

CLAIMS

1. A process to manufacture from rock phosphate commercially acceptable phosphoric acid and gypsum comprising reacting coarser samples of rock phosphate with a mixture of phosphoric acid and fluosilicic acid with a minute quantity of sulphuric acid at a temperature from ambient to 100°C. 5 until the phosphate and fluorine contents in the rock phosphate are substantially dissolved, the resulting slurry being fed into a crystalliser containing slurry from previous batch, the slurry being reacted in the crystalliser with sulphuric acid, the reaction in the crystalliser being continued till gypsum crystal formation is complete, the crystalliser contents being 10 filtered and the residue containing substantially gypsum crystals being washed several times, the filtrate and washings containing a mixtures of phosphoric acid:fluosilicic acid, being divided into two unequal portions, the smaller portion containing P_2O_5 "equivalent" to that contained in the rock phosphate at the beginning of the process, the smaller portion 15 being concentrated to give phosphoric acid, the fluosilicic acid evolved during the concentration process being scrubbed and mixed with the larger portion, the last mentioned mixture being recycled to a fresh quantity of rock phosphate to repeat the process.
2. A process to manufacture from rock phosphate commercially acceptable 20 phosphoric acid and gypsum as claimed in Claim 1 wherein the slurry produced by the reaction of rock phosphate with the mixture of phosphoric acid and fluosilicic acid containing a minute quantity of sulphuric acid is filtered to removed insoluble impurities and the filtrate and washings of the residue are fed into the crystalliser containing slurry from previous 25 batch.

3. A process to manufacture from rock phosphate commercially acceptable phosphoric acid and gypsum as claimed in claim 2, wherein the filtrate and washings of the residue are divided into two portions, the smaller portion containing P_2O_5 "equivalent" to that contained in the rock phosphate. At the beginning of the process, the smaller portion being concentrated and cooled and filtered, the residue being wet calcium silicofluoride and the filtrate being product phosphoric acid, the cake of wet calcium silicofluoride being added to the aforesaid larger portion in a crystalliser containing slurry from previous batch and sulphuric acid being added into the crystalliser, the reaction in the crystalliser being continued till the gypsum crystal formation is complete, the gypsum crystals being filtered and washed, the filtrate being recycled to a fresh quantity of rock phosphate to repeat the process.

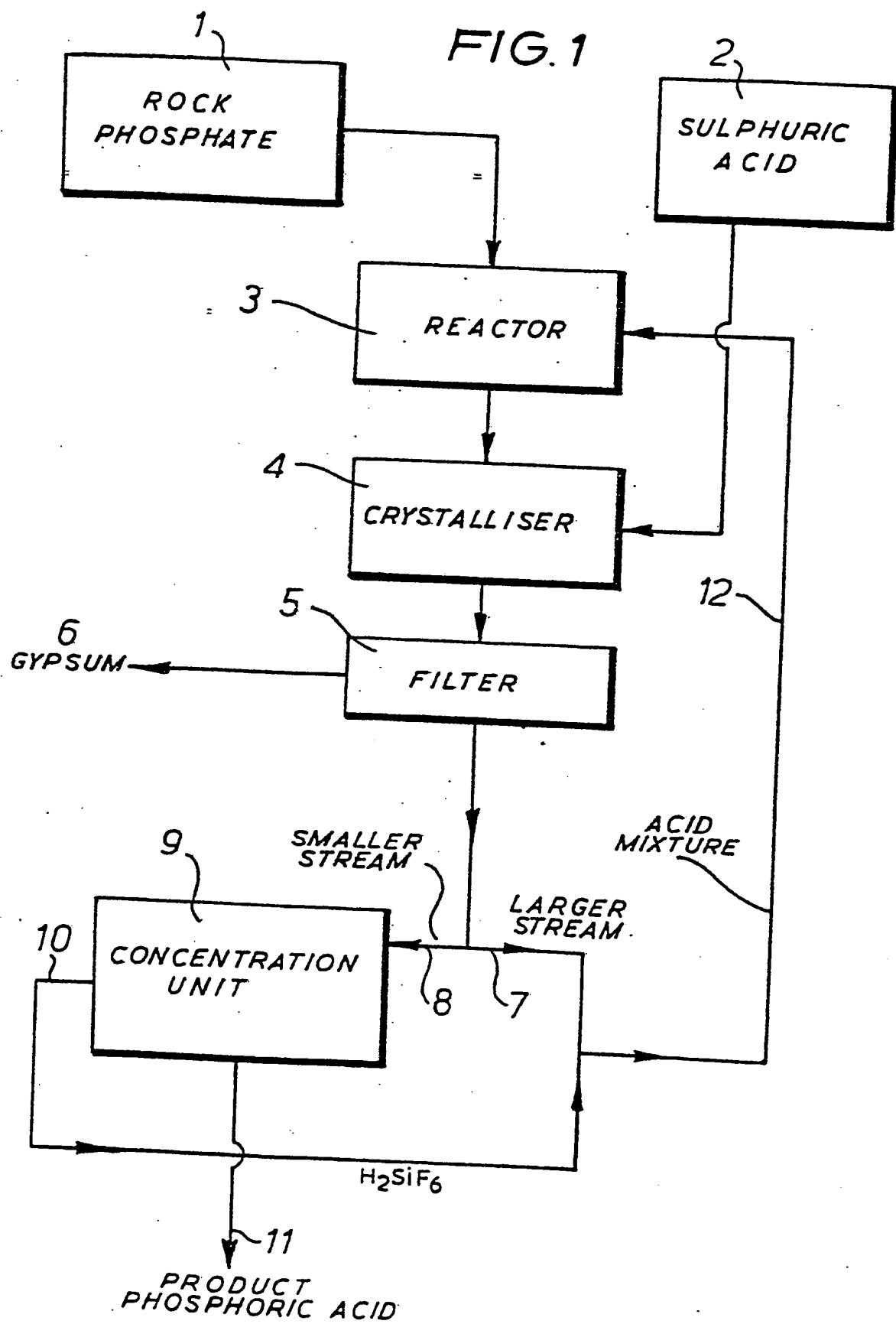
4. A process for the manufacture of gypsum and phosphoric acid from rock phosphate, which process comprises treating rock phosphate with fluosilicic acid optionally together with phosphoric acid to solubilise the phosphate content thereof, regenerating fluosilicic acid and precipitating gypsum by treating at least part of the product so obtained with sulphuric acid, separating out the gypsum, separating out product phosphoric acid and re-cycling the regenerated fluosilicic acid to treat further rock phosphate.

5. A process as claimed in claim 4, wherein at least part of the solution obtained from the solubilisation step is concentrated until calcium silicofluoride precipitates.

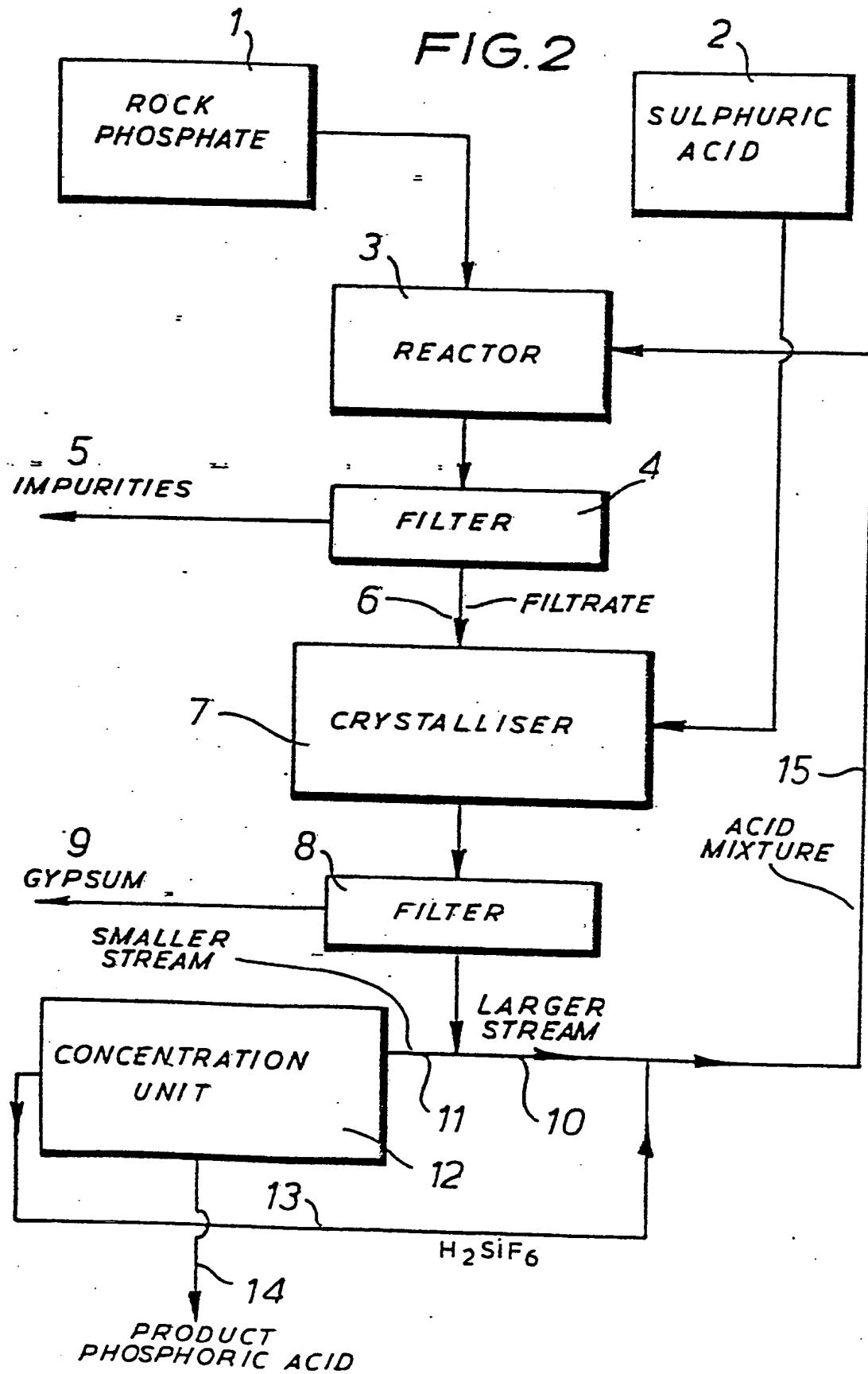
6. A process as claimed in claim 5, wherein only a portion of the solution obtained from the solubilisation step is concentrated to precipitate calcium silicofluoride, the mother liquor remaining after precipitation
- 5 constituting the product phosphoric acid and the precipitated calcium silicofluoride being passed to the sulphuric acid treatment step.
7. A process as claimed in claim 4, wherein substantially the whole of the solution obtained from the dissolution
- 10 step is treated with sulphuric acid and the gypsum precipitated thereby is separated from the slurry so obtained.
8. A process as claimed in claim 7, wherein the product phosphoric acid is derived by scrubbing at least a portion
- 15 of the liquor remaining after the sulphuric acid treatment step.
9. A process as claimed in any one of claims 4 to 8, wherein the product of the solubilisation step is filtered to remove undissolved impurities prior to the sulphuric
- 20 acid treatment.
10. Phosphoric acid and/or gypsum obtained from a process as claimed in any one of claims 1 to 9.

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FIG. 1

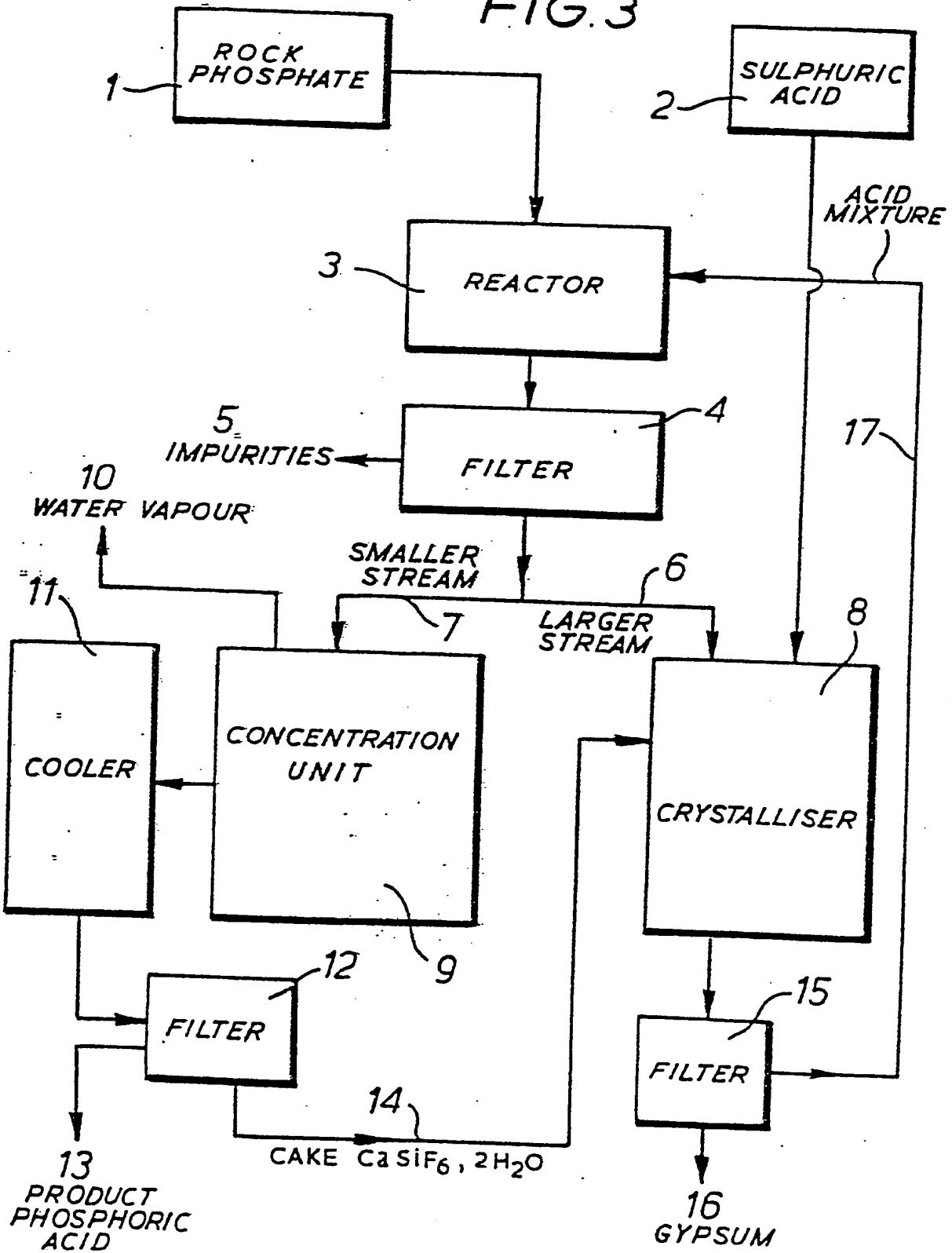


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FIG. 3





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ?)
A	US-A-2 636 806 (E.A. WINTER) * Figure; claims 1,5,10,11 *	4,5,9	C 01 B 25/22 C 01 F 11/46
A	--- CHEMICAL ABSTRACTS, vol. 64, no. 9, 25th April 1966, columns 12234h-12235b, Columbus, Ohio, USA S.Y. SHPUNT: "Production of phosphoric acid by decomposition of Mg-containing phosphate ores with H ₂ SiF ₆ " & KHIM. PROM. 41(9), 674-8(1965) * Whole abstract *	4	
A	--- CHEMISCHES ZENTRALBLATT, vol. 138, no. 45, 8th November 1967, page 238, article no. 2050, Berlin & Weinheim, DE. S.J. SPUNT et al.: "Gewinnung von Phosphorsäure durch Zerlegung von magnesiumhaltigen Phosphoriten mit Siliciumfluorwasserstoffsäure" * Whole abstract *	4	
	---	-/-	TECHNICAL FIELDS SEARCHED (Int. Cl. ?)
			C 01 B 25/00
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	29-04-1983	BREBION J.C.H.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
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P : intermediate document	& : member of the same patent family, corresponding document		



DOCUMENTS CONSIDERED TO BE RELEVANT			Page 2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. *)
A	<p>CHEMICAL ABSTRACTS, vol. 69, no. 14, 30th September 1968, page 4985, no. 53237p, Columbus, Ohio, USA</p> <p>K.I. MAKAR'IN et al.: "Preparation of concentrated phosphoric acid from Kara-Tau phosphorites" & IZV. VYSSH. UCHEB. ZAVED., KHIM. KHIM. TEKKNOL. 1968, 11(3), 313-16 * Whole abstract *</p> <p>---</p> <p>TECHNICAL DIGEST, vol. 10, no 12, December 1968, page 840, Prague, CS.</p> <p>"Manufacture of concentrated phosphoric acid from hard-to-decompose phosphorites" * Whole articel *</p> <p>---</p> <p>CHEMICAL ABSTRACTS, vol. 71, no. 16, 20th October 1969, page 154, no. 72441h, Columbus, Ohio, USA</p> <p>K.I. MAKAR'IN et al.: "Production of phosphoric acid" & OTKRYLIYA, IZOBRET., PROM. OBRAZTSY, TOVARNYE ZNAKI, 1969, 46(15), 22 * Whole abstract *</p> <p>---</p>	4,5	
A		4,5	
A		4,5	TECHNICAL FIELDS SEARCHED (Int. Cl. *)
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 29-04-1983	Examiner BREBION J.CH.	
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>	
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DOCUMENTS CONSIDERED TO BE RELEVANT

Page 3

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
A	CHEMICAL ABSTRACTS, vol. 72, no. 22, 1st June 1970, page 129, no. 113315m, Columbus, Ohio, USA S.Y. SHPUNT: "Continuous methods for preparing concentrated phosphoric acid and fertilizers based on the decomposition of phosphates by fluorosilicic and hydrofluoric acids" & KHIM. PROM. (MOSCOW), 1970, 46(1), 28-33 * Whole abstract *	4	
A	--- CHEMICAL ABSTRACTS, vol. 84, no. 18, 3rd May 1976, page 127, no. 123995v, Columbus, Ohio, USA H. LLOYD BANNING: "Fluosilicic acid acidulation of phosphate rock" & U.S., BUR. MINES, REP. INVEST. 1975, RI 8061, 13pp. * Whole abstract *	4	
A	--- CHEMICAL ABSTRACTS, vol. 97, no. 21, 22th November 1982, page 711, no. 181101e, Columbus, Ohio, USA A.A. ZATOUT et al.: "Fluosilicic acid acidulation of Egyptian Abu-Tartur rock phosphate" & Fert. TECHNOL., 1981, 18(1-2), 95-8	4	TECHNICAL FIELDS SEARCHED (Int. Cl. 5)
A	--- FR-A- 633 828 (F.G. LILJENROTH) * Abstract 2b; page 2, lines 35-43, example 1 *	4	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	29-04-1983	BREBION J.C.H.	
CATEGORY OF CITED DOCUMENTS			
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